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BANDAGING MATERIAL OR NAPKIN, IN PARTICULAR A SANITARY NAPKIN OR TAMPON, MADE OF A LIQUID-ABSORBING MATERIAL

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Printed documents taken into consideration for evaluating the patentability:

German Patent Nos. 714,870 and 965,593; Schweizer Apotheker-Zeitung 93, 1955, pp. 33-36

The subject matter of this invention concerns a bandaging material or a napkin, in particular a sanitary napkin or a tampon, made of a liquid-absorbing material.

It is a well-known fact that water-soluble cellulose ethers, especially salts of carboxymethylcellulose, can be used as water-absorbing bandaging material. However, these water-soluble products have the disadvantage that they swell only slightly when they come into contact with liquids and that they are at least in part definitely dissolved and leached out by body fluids, such as blood. Sanitary napkins or tampons on the basis of such water-soluble cellulose ethers of corresponding water-soluble salts have therefore often been responsible for soiling clothes.

It was discovered that bandaging materials or napkins, in particular sanitary napkins or tampons, made of a liquid-absorbing material which contains salts, in particular sodium salts of carboxyalkylcellulose, preferably sodium salts of carboxymethylcellulose, have excellent properties if the cellulose has a degree of etherification of 0.05 to 0.3. Napkins or tampons may consist completely of the alkali salts of

carboxyalkylcellulose mentioned. Especially satisfactory products are obtained when the salt of carboxyalkylcellulose is mixed with other water-absorbing materials, such as unsubstituted cellulose, e.g., cotton linters.

The degree of etherification of cellulose is determined by the average number of hydroxyl groups per anhydroglucose unit on which a chemical addition took place.

During the formation of sodium carboxymethylcellulose, the carboxymethyl groups attach themselves to the hydroxyl groups of the cellulose while forming ether bonds, i.e., while etherification takes place. According to this definition, the degree of etherification in sodium carboxymethylcellulose can at most reach a value of 3 since the anhydroglucose units of the cellulose molecule have three free hydroxyl groups.

The manufacture of sodium carboxymethylcellulose which is the main component of the bandaging material according to this invention is well known. Bandaging materials or napkins which contain salts with the degree of etherification mentioned above remain insoluble when they come into contact with body fluids, such as secretions.

Sanitary napkins according to this invention may be produced in the form of oblong pads to be worn externally or in the form of tampons. A short string is generally attached to the latter; this string may be wound around the core of the tampon before it is completely enclosed with the absorbent material (see U.S. Patent Specification No. 2,123,750). The string remains outside the vaginal entrance and can be pulled when the tampon is to be removed.

In mixtures of unmodified cellulose and practically water-insoluble sodium carboxymethylcellulose, the quantity ratio of the two components is irrelevant. But the absorptive capacity of the material is definitely improved by the addition of such celluloseglycolates. Unsubstituted cellulose may also be added in the form of purified lignocellulose, etc. Long-fiber cotton linters are preferred because of their soft hand and because the sodium carboxymethylcellulose is preferably also produced from long-fiber cotton linters which may be etherified by means of the method described in Example 1.

In contrast with the individual components, mixtures of sodium carboxymethylcellulose and unsubstituted cellulose are, as already mentioned earlier, superior with respect to the liquid-absorbing capacity. This is probably attributable to a crosslinking effect of the unsubstituted cellulose.

The figures in Table I document the superior absorptive qualities of mixtures of sodium carboxymethylcellulose (CMC) and of mixtures thereof with unsubstituted cellulose when compared to the materials that consist only of cellulose. When absorbing liquids, sodium carboxymethylcellulose (CMC) swells to a considerably greater degree than unsubstituted cellulose, with the result that tampons made of sodium carboxymethylcellulose are much better able to swell in and fill the vagina. Body fluids can therefore not flow past the tampons and exit from the vagina.

Sodium carboxymethylcellulose with a degree of etherification lower than 0.05 has properties that are substantially similar to those of unsubstituted cellulose and is therefore of no interest to this invention. At a degree of etherification higher than approximately 0.3, sodium

carboxymethylcellulose becomes water-soluble and is therefore also of no use in the context of this invention. The water-solubility depends on a uniform substitution, on the one hand, and on the degree of etherification, on the other hand.

The absorptive capacity of various materials for water was tested by compressing 1 g of each material in a tablet-compressing machine to a density of 0.3 g/cm³. Each of these 1 g samples was held by a clamp and immersed for a certain length of time in a container filled with water. The table below summarizes the data obtained with unsubstituted cellulose, for various types of sodium carboxymethylcellulose (CMC), and for a mixture of unsubstituted cellulose and sodium carboxymethylcellulose (CMC).

Table I

	1 Muster-Nr.						
	1	2	3	4	5	6	7
2 Art des Stoffes	Cellulose	CMC	0,5 Cellulose +0,5 CMC	CMC	CMC	CMC	CMC
3 Verätherungsgrad	0	0,23	0.23*	0.05	0.10	0.20	0.27
4 Tauchzeit (Minuten)	5	5	5	10	10	10	10
5 Wasserabsorption (g)	1,4	2,3	3,6	3.5	5,5	6,0	7,8

* In this context, degree of etherification refers to the sodium carboxymethylcellulose used prior to mixing it with cellulose.

Key: 1 = Sample No.
2 = Type of material
3 = Degree of etherification
4 = Duration of immersion (minutes)
5 = Water absorption (g)

The carboxymethylcellulose (CMC) used in Sample 4 had been prepared as follows (the quantities given refer to the weight):

In a bottle with a volume of 9.1 L, 1520 g of xylene, 293 g of ethyl alcohol, 90 g of water, and 100 g of cellulose were agitated for 5 minutes. The bottle was closed with a metal cap that was coated with polyethylene. A narrow glass tube extended through the center of this cap into the bottle.

Subsequently, 9.4 g of sodium hydroxide were added to the mixture which was again agitated for 30 more minutes by rotating it back and forth. At intervals of 10 minutes, the cellulose was reduced to fibers and kneaded to ensure that all reaction participants were thoroughly blended. After the addition of 9.5 g of monochloroacetic acid to the mixture, the mixture was again agitated by rotating it back and forth for 10 minutes. Subsequently, it was heated to 50°C to 60°C in a water bath and again agitated by rotating it back and forth for 15 to 20 minutes. Alternately heating and agitating the mixture continued for a total of 3 hours. Subsequently, the reaction mixture was neutralized with acetic acid and washed with a mixture of 65 parts of alcohol and 35 parts of water.

The sodium carboxymethylcellulose of Samples 5, 6, and 7 of the preceding Table I were similarly prepared, except that different quantities of alkali hydroxide and monochloroacetic acid were used.

The reference experiments described below demonstrate that mixtures consisting of 50% of unmodified cellulose and 50% of a sodium carboxymethylcellulose with a degree of etherification of 0.8, i.e, with a water-soluble product, have a considerably lower absorptive capacity than similar mixtures consisting of 50% of

unmodified cellulose and 50% of sodium carboxymethylcellulose with a degree of etherification of 0.29 as described by this invention. The tests were carried out while the mixtures were moved around to ensure that the actual conditions during practical application were approached as much as possible.

It was also demonstrated that the water-soluble sodium carboxymethylcellulose was largely dissolved out of the mixtures but that only a small portion of the water-insoluble sodium carboxymethylcellulose was affected. In addition, the data summarized in Table II clearly demonstrate that the mixtures containing the water-insoluble product absorb approximately 50% more water per gram of mixture when the measurement of the remaining water content is carried out without squeezing the water out of the mixture. When the absorption is measured after the water has been squeezed out of the mixture, data indicate that as much as approximately 60% more water had been absorbed.

First, two mixtures of unmodified long-fiber cotton and sodium carboxymethylcellulose were prepared.

Mixture a) consisted of 50% of this unmodified cotton and 50% of a completely water-soluble sodium carboxymethylcellulose made from this cotton and having a degree of etherification of 0.8.

Mixture b) consisted of 50% of the unmodified long-fiber cotton and 50% of a water-insoluble sodium carboxymethylcellulose made from this cotton and having a degree of etherification of 0.29.

The mixtures were placed into a bag made of coarse cotton with a volume of 7.5 cm^2. Three individual samples of each

mixture were attached to disks of a vertically standing and oscillating shaft. For 1 hour, the samples were moved approximately 84 times per minute at an angle of 120° through a water bath. After 1 hour, the samples were removed from the water and dried for one hour. (In blind tests, identical bags made of coarse cotton were subjected to the same treatment in order to determine their average weight for control purposes.) Subsequently, the samples were weighed; the values measured are listed in Table II in the column "Absorption of fluid in g of H_2O/g of mixture used (determined without squeezing the water out of the material)."

The weighed samples were subsequently subjected for 15 minutes to a pressure of 0.035 kg/cm^2 and then weighed again. The data obtained are listed in Table II in the column "Absorption of fluid in g of H_2O/g of mixture used (determined after squeezing the water out of the material)."

Finally, the remaining samples were removed from the bags and dried for 3 hours at 100°C. The samples were subsequently allowed to dry to ambient temperature while cooling them slowly. They were then weighed again. The data obtained are listed in Table II in the column "Remaining percentage of the mixture used (percent by weight)."

Table II

Reference tests with 50:50 mixtures of unmodified cotton with
a) highly etherified water-soluble sodium carboxymethylcellulose and
b) low-etherified water-insoluble sodium carboxymethylcellulose

1 Art der Natriumcarboxymethylcellulose in der Mischung	2 Flüssigkeitsabsorption in g H_2O/g eingesetzter Mischung (ohne Ausdrücken bestimmt)		3 Flüssigkeitsabsorption in g H_2O/g eingesetzter Mischung (mit Ausdrücken unter 0,035 kg/cm² Überdruck bestimmt)		4 Zurückbleibende Anteile der eingesetzten Mischung (Gewichtsprozent)	
5 1. Hochverätherte wasserlösliche Natriumcarboxymethylcellulose (Verätherungsgrad 0,8)	(1)	12,8	(1)	10,0	(1)	48
	(2)	13,2	(2)	10,0	(2)	49
	(3)	15,2	(3)	11,8	(3)	47
	7 Durchschnitt	13,7	7 Durchschnitt	10,6	7 Durchschnitt	48
6 2. Niedrigverätherte wasserunlösliche Natriumcarboxymethylcellulose der Erfindung (Verätherungsgrad 0,29)	(1)	20,7	(1)	16,7	(1)	70
	(2)	19,6	(2)	15,8	(2)	74
	(3)	19,9	(3)	18,5	(3)	68
	7 Durchschnitt	20,1	7 Durchschnitt	17,0	7 Durchschnitt	71

Key:
1 = Type of sodium carboxymethylcellulose contained in the mixture
2 = Absorption of fluid in g of H_2O/g of mixture used (determined without squeezing the water out of the material)
3 = Absorption of fluid in g of H_2O/g of mixture used (determined after squeezing the water out of the material using a pressure of 0.035 kg/cm^2)
4 = Remaining percentage of the mixture used (percent by weight)
5 = 1. Highly etherified water-soluble sodium carboxymethylcellulose (degree of etherification 0.8)
6 = 2. Low-etherified water-insoluble sodium carboxymethylcellulose according to this invention (degree of etherification 0.29)
7 = Average

Patent Claims

1. Bandaging material or a napkin, in particular a sanitary napkin or a tampon, made of a liquid-absorbing material containing salts, in particular sodium salts of carboxyalkylcellulose, preferably sodium salts of carboxymethylcellulose, characterized by the fact that the cellulose has a degree of etherification of 0.05 to 0.3.

2. Bandaging material according to Claim 1, characterized by the fact that the salt of the carboxyalkylcellulose is mixed with another water-absorbing material, such as unsubstituted cellulose, e.g., cotton linters.